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Application of Scanning Tunneling Microscopy to Studies of Electrode Surfaces.

by

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13. ABSTRACT *(Maximum 200 words)*
This project involved the study of a variety of different surfaces and structures in gaseous and liquid environments using the scanning tunneling microscope (STM) and other scanning probe microscopes with the aim of obtaining a better understanding of electrode surfaces and the processes occuring on these surfaces. With the STM we investigated chemical changes on the surface of electrodes, e.g., corrosion, passivation, and biochemical activities, and studied the energetics for electron transfer at the surfaces of semiconductors. We also investigated nanostructures (for example, very small semiconductor particles, porous Si, and self-assembled monolayers) using this technique.

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Summary

This project involved the study of a variety of different surfaces and structures in gaseous and liquid environments using the scanning tunneling microscope (STM) and other scanning probe microscopes (SPM's) with the aim of obtaining a better understanding of electrode surfaces and the processes occuring on these surfaces. With the STM we investigated chemical changes on the surface of electrodes, e.g., corrosion, passivation, and biochemical activities, and studied the energetics for electron transfer at the surfaces of semiconductors. We also investigated nanostructures (for example, very small semiconductor particles, porous Si, and self-assembled monolayers (SAM)) using this technique.

In the final year of this project, SPM's were used to study several interesting electrochemical problems. (1) SAM on Au(111). In our continued study of the packing of alkylthiols on the Au substrate, the formation of multilayers was observed when the Au substrates were immersed in a solution containing alkylthiols for more than 4-5h. (2) Corrosion of Ni(001) in 1 M NaOH. We used the STM to examine the anodic oxides formed on Ni(001) under potential control in 1 M NaOH. Atomic images of nickel oxides were obtained and the dynamics of oxide film growth were observed. (3) Porous Silicon. SPM, XPS, FTIR, and laser ionization microanalysis (LIMA) techniques have been used to examine the surface morphology and chemical nature of porous silicon. The results suggest that the photoluminescence from porous Si might be caused by a chemically modified layer on the surface. (4) Enzyme microelectrodes for the scanning electrochemical microscope. We demonstrated that the utilization of horseradish peroxidase microelectrodes can be used for mechanistic studies of oxygen reduction and the the detection of immobilized oxidases without the need for artificial redox mediators. (5) Cu(111) Dissolution in aqueous chloride. In situ STM analysis was used to ascertain the mechanism of the anodic dissolution of Cu(111) in aqueous chloride media with atomic resolution. STM imaging at potentials where Cu dissolution begins revealed that the preferred reaction sites were step edges, and that the retreating edges ran along steps in the {211} direction.

Personnel Supported by N00014-91-J-1752

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Publications in Refereed Journals

C.-Y. Liu, H. Chang and A. J. Bard, "Large Scale Hexagonal Domainlike Structures Superimposed on the Atomic Corrugation of a Graphite Surface Observed by Scanning Tunneling Microscopy," Langmuir, 7, 1138 (1991).

H. Chang and A. J. Bard, "Observation and Characterization by Scanning Tunneling Microscopy of Structures Generated by Cleaving Highly Oriented Pyrolytic Graphite," Langmuir, 7, 1143 (1991).

Y.-T. Kim, H. Yang, and A. J. Bard, "Electrochemical Control of Polyaniline Morphology as Studied by Scanning Tunneling Microscopy," J. Electrochem. Soc., 138, L71 (1991).

J. Sarathy, S. Shih, K. Jung, C. Tsai, K.-H. Li, D.-L. Kwong, J. C. Campbell, S.-L. Yau, and A. J. Bard, "Demonstration of Photoluminescence in Nonanodized Silicon," Appl. Phys. Lett., 60, 1532 (1992).

P. McCord, S.-L. Yau, and A. J. Bard, "Chemiluminescence of Anodized and Etched Silicon: Evidence for a Luminescent Siloxene-Like Layer on Porous Silicon," Science, 257, 68 (1992).

1) This study and related ones listed in the publications list focused on the anodic etching of silicon and the nature of the porous silicon that forms on a silicon surface. A number of techniques, including STM, were used to characterize the silicon surface, and it was demonstrated in this paper for the first time that one can obtain chemiluminescent reactions of the porous silicon layer. This strongly suggests the presence of a silicon compound with hydrogen and oxygen as the source of the visible emission.

H. Yang, F.-R. F. Fan, S.-L. Yau, and A. J. Bard, "The Use of a Scanning Tunneling Microscope to Estimate Film Thickness and Conductivity of an Electrochemically Produced Poly-1-aminoanthracene Film," J. Electrochem. Soc., 139, 2182 (1992).

R. L. McCarley and A. J. Bard, "Surface Reactions of Au(111) with Aqueous Cyanide Studied by Scanning Tunneling Microscopy," J. Phys. Chem., 96, 7410 (1992).

Y. -T. Kim, R. L. McCarley, and A. J. Bard, "Scanning Tunneling Microscopy Studies of Au(111) Derivatized with Organothiols," J. Phys. Chem., 96, 7416 (1992).

S.-L. Yau, T. P. Moffat, A. J. Bard, Z. Zhang, and M. M. Lerner, "STM of the (010) Surface of Orthorhombic Phosphorus," Chem. Phys. Lett., 198, 838 (1992).

S. A. Hendricks, Y.-T. Kim, and A. J. Bard, "Imaging of the In Situ Deposition of Lead on Highly Oriented Pyrolytic Graphite by Scanning Tunneling and Atomic Force Microscopies," J. Electrochem. Soc., 139, 2818 (1992).

S.-L. Yau, F.-R. F. Fan, and A. J. Bard, "*In Situ* STM Imaging of Silicon(111) in HF under Potential Control," J. Electrochem. Soc., 139, 2825 (1992).

C. Tsai, K.-H. Li, J.C. Campbell, M. F. Arendt, B. K. Hance, J. M. White, S.-L. Yau, and A. J. Bard, "Effects of Illumination During Anodization on Porous Silicon," J. Electronic Materials, 21, 995 (1992).

T. P. Moffat, H. Yang, F.-R. F. Fan, and A. J. Bard, "Electron Transfer Reactions on Passive Chromium," J. Electrochem. Soc., 139, 3158 (1992).

R. L. McCarley, S. A. Hendricks, and A. J. Bard, "Controlled Nanofabrication of Highly Oriented Pyrolytic Graphite with the Scanning Tunneling Microscope," J. Phys. Chem., 96, 10089 (1992).

F.-R. F. Fan and A. J. Bard, "Photoassisted Scanning Tunneling Microscopy and Tunneling Spectroscopy of n-Type Tungsten Diselenide (n-WSe_2) Single Crystals," J. Phys. Chem., 97, 1431 (1993).

2) We demonstrate here that one can image resistive semiconductors by irradiating the semiconductor; thus, information about the energy levels and band gap of these materials can be obtained

Y.-T. Kim, R. L. McCarley, and A. J. Bard, "Observation of n-Octadecanethiol Multilayer Formation from Solution onto Gold," Langmuir, 9, 1941 (1993).

A. J. Bard and F.-R. Fan, "Studies of the Liquid/Solid Interface by Scanning Tunnelling Microscopy and Scanning Electrochemical Microscopy," Faraday Discuss., 94, 1 (1992). [Published in 1993.]

B. R. Horrocks, D. Schmidtke, A. Heller, and A. J. Bard, "Scanning Electrochemical Microscopy. 24. Enzyme Ultramicroelectrodes for the Measurement of Hydrogen Peroxide at Surfaces," Anal. Chem., 65, 3605 (1993).

S.-L. Yau, M. Arendt, A. J. Bard, B. Evans, C. Tsai, J. Sarathy, and J. C. Campbell, "Study of the Structure and Chemical Nature of Porous Si and Siloxene by STM, AFM, XPS, and LIMA," J. Electrochem. Soc., 141, 402 (1994).

S.-L. Yau, F.-R. Fan, T. P. Moffat, and A. J. Bard, "In Situ Scanning Tunneling Microscopy of Ni(100) in 1 M NaOH," J. Phys. Chem., 98, 5493, (1994).

3) There have been relatively few studies of active metals exposed to an aqueous environment. Studies of this sort are of interest in probing surface films that form on metals during corrosion and the atomic level mechanism of corrosion processes. This paper is one of the earliest examples of such a study, which allowed atomic resolution imaging of nickel and nickel oxides.

Submitted:

D. Wayne Suggs and Allen J. Bard, "Scanning Tunneling Microscopic Study with Atomic Resolution of the Dissolution of Cu(111) in Aqueous Chloride Solutions," *J. Am. Chem. Soc.*

Invited Presentations:

"Studies of the Liquid-Solid Interface by STM and Scanning Electrochemical Microscopy," The Royal Society of Chemistry, Faraday Division, General Discussion No. 94, University of Newcastle Upon Tyne, Newcastle, UK, September 7, 1992.

I was invited to give the introductory lecture at a Faraday discussion devoted to the liquid/solid interface at high resolution. In the lecture I discussed the general nature of the interface and gave a number of examples based on our recent work on the use of scanning probe microscopy in characterizing this interface.

"Ultrahigh Resolution Surface Analysis by Scanning Tunneling Microscopy and Scanning Electrochemical Microscopy," Pittsburgh Conference, Atlanta, Georgia, March 8, 1993.

"Scanning Probe Microscopy of Electrode Surfaces," Royal Society of Chemistry Congress, Liverpool, England, April 13, 1994.

Honors/Awards/Prizes:

G. M. Kosolapoff Award, American Chemical Society (Allen J. Bard)

Luigi Galvani Medal, Societá Chimica Italiana (Allen J. Bard)

I was fortunate to receive the Galvani medal from the Italian Chemical Society recognizing our research in the general area of electrochemistry. The lecture discussed scanning probe microscopy as applied to electrochemical problems.

Other Funding:

Robert A. Welch Foundation. Ultrahigh Resolution Electrochemistry. Current year: $52,000. Total award: $156,000. 6/1/94 - 5/31/97.

National Science Foundation. Mechanisms of Electrode Reactions. Current year: $150,000. Total award: $470,000. 6/1/92 - 4/30/95.

National Science Foundation. Photoelectrochemistry and Heterogeneous Photoprocesses at Semiconductors. Current year: $120,000. Total award: $395,795. 1/1/92 - 12/31/94.

Texas Instruments. Electro-optical Memory Devices Based on Novel Thin-film Materials. Total award: $100,000. 1/1/93 - 12/31/97.

Army Research Office (subcontracted through the University of Delaware). Molecular Interactions and Reaction Dynamics in Supercritical Water Oxidation. Joint project with Professors K. P. Johnston and M. A. Fox. Total award for 3 PI's: $1,330,705. Current year, A. J. Bard: $45,898. Total award, A. J. Bard: $230,211. 7/1/92 - 6/30/97.

Advanced Research Program. Advanced Electrogenerated Chemiluminescent Systems. Total Award: $79,880. 1/1/94 - 12/31/95.

IGEN. Electrogenerated Chemiluminescence. Total Award: $45,000.

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